



Maria S. Merian Cruise 1 leg 3

Fourth weekly report: 03. 05. - 09. 05. 2006

We left Cadiz on Wednesday (03.05) at 19:50h and headed back to Captain Arutyunov MV (CAMV) with a service technician from IXSEA on board. We stopped our transit to CAMV some miles off the MV where we deployed a POSIDONIA transponder on a short mooring at 1160m depth in order to calibrate the newly installed POSIDONIA System. The calibration proceeded routinely. However, when we tried to retrieve the mooring with the POSIDONIA transponder the mooring did not swim up although the acoustic releases had confirmed the release from the anchor weight. We decided to postpone any salvage operation and steamed to CAMV where we successfully retrieved the BIGO lander deployed on Monday (01.05). We headed back to the mooring side and decided to salvage the mooring with the OFOS equipped with some short draglines and hooks. Another POSIDONIA beacon on the OFOS enabled a precise navigation of the OFOS and concurrently turned out as an excellent test for the functioning of the POSIDONIA system. In consequence we could spot the anchor weight with the first deployment of OFOS and with the help of the outstanding manoeuvrability of the ship we were able to push OFOS against the mooring next to the release transponders and thus to set free the entangled acoustic releases. The mooring swam up immediately after the first impact and could be retrieved safely. We then headed back to the pilot station to disembark the IXSEA service technician and to take in a journalist from a pilot boat who will report about our activities from Leg 3b. A web log about MSM 1-3b is installed on the home page of the Deutsche Welle : www.dw-world.de (search under: dw tv / „was gibt's" / Sendungen / Projekt Zukunft or Tomorrow Today

We steamed back to CAMV and continued station work. The FLUFO Lander was deployed "right within a crater of mud flow" and for the first time the PWPL Lander (Pore Water Pressure Lance) only 6m apart from FLUFO (Fig. 1b). The PWPL carries a pore water lance of two metres length which is driven by a motor into the sediment. With this deployment we finished our station work at CAMV and steamed east towards the region of the shallow Moroccan mud volcanoes. Our first target was the Mercator MV where we started with a comprehensive OFOS survey in order to identify areas of enhanced biological activity triggered by methane flow. We could visualize methane bubbles near the top of the MV. We also enlarged our investigation box to the adjacent Renard Ridge and performed an OFOS survey at the Pen Duick escarpment to detect coral occurrences on a transect perpendicular to the ridge. We left the area again to revisit CAMV where we deployed the BIGO Lander at the gas hydrate site and retrieved three landers from the top of CAMV: DOS Lander, FLUFO Lander and PWPL Lander. Afterwards we steamed back to Renard Ridge and started an intensive OFOS survey on the western crest of the ridge where massive occurrence of dead *Lophelia* reefs were detected. On Monday night we headed further south to the Mekenese MV near 35°N and mapped the area with multi beam.

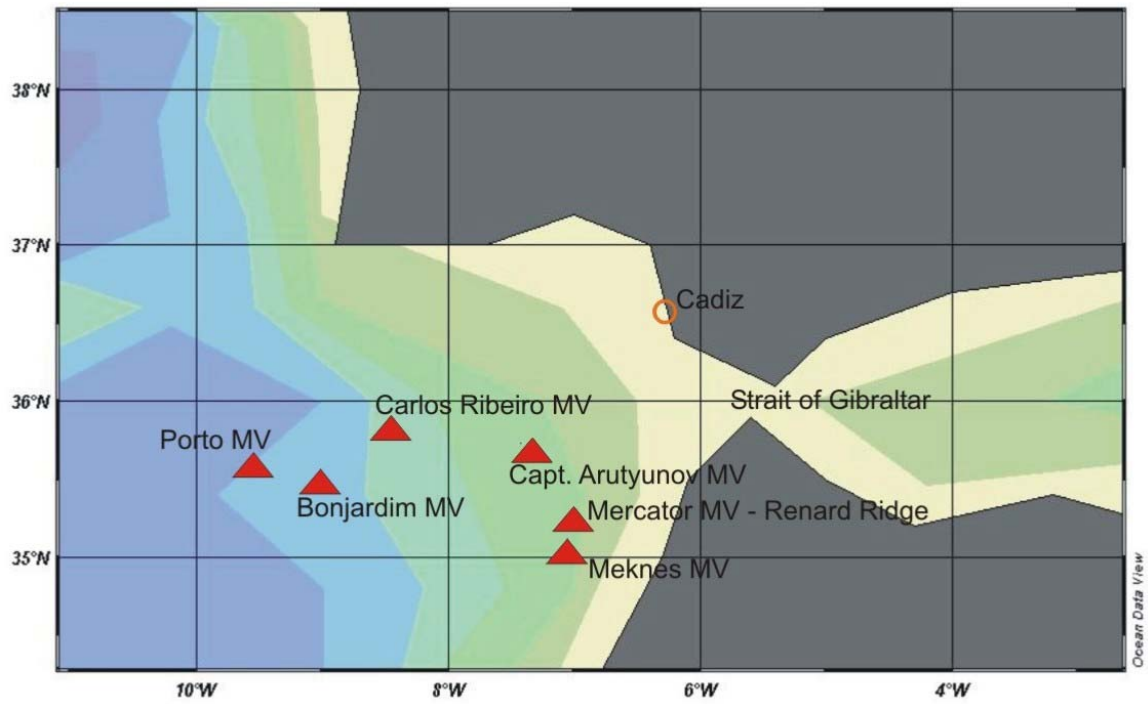


Fig. 1a: Working area with positions of the surveyed mud volcanoes.

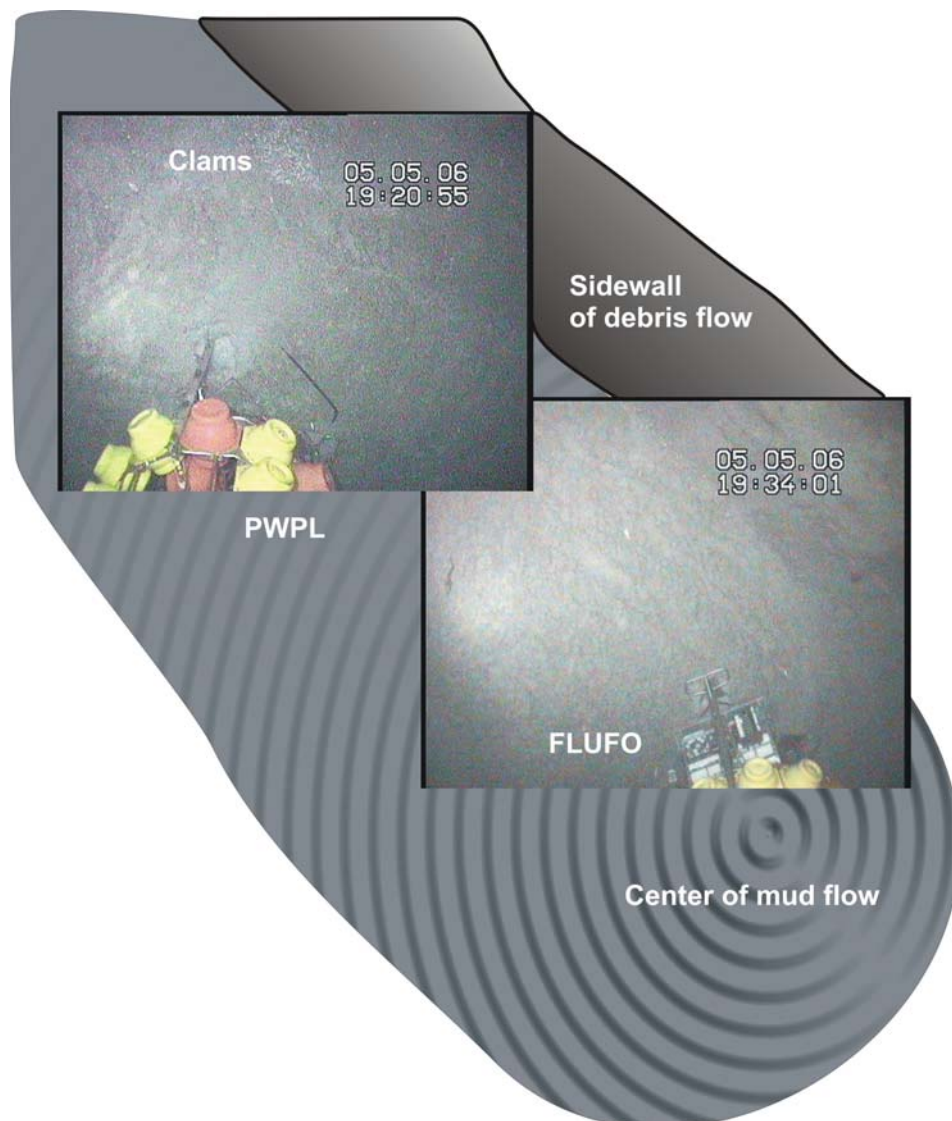


Fig. 1b: Illustration of the CAMV site

The hydrographic regime at CAMV was studied in detail and can be described as follows: Situated at a water depth between 1420 and 1312m, the top of the mound lies well below the lower tongue of the Mediterranean Outflow Water (MOW). The aim of the CTD casts was to investigate possible relations between physical properties and spatial variability of water masses and the occurrence of cold water corals at the mound which were sampled with the TV-Grab.

High-resolution CTD measurements (potential temperature, salinity, density, and dissolved oxygen) in the working area allowed the identification of the main water masses present in the study area. The potential temperature versus salinity multiplots of the CTD casts show the following hydrological structure (see Figure 2): (a) the upper surface layer (0- ~170m); (b) the permanent thermo-halocline, corresponding to the North Atlantic Central Water (NACW) between ~170-700m; (c) the two layers of warm and salty MOW at ~780 and 1200m; and the (d) the presence of North Atlantic Deep Water (NADW) associated with depth-decreasing thermocline properties.

A total of 13 CTD/Ro casts have been carried out in 5 days which spanned over two full tidal cycles covering ~ 24 hours. The measurements indicate strong variation of water masses between 250 and 1250 meters. The greatest changes occur within the upper and lower core of the MOW suggesting either tidal influence or varying outflow from the Strait of Gibraltar. Closer analysis of weather patterns in the study area and the Alboran Sea will be used to investigate these two options. Changing pressure systems have already been identified to influence Mediterranean outflow (W. Zenk; pers. comm.). Analysis of the distribution of potential temperature and salinity indicate variable water masses. The greatest variation occurs within the two cores of the high saline and warm MOW. In the upper core salinity varies between 35.85 and 36.09, whereas salinity in the lower core ranges from 35.99-36.10. At the same time the depth of the salinity maxima varies between 761 and 816m for the upper core and 1128 and 1209m for the lower core. For the analysed parameters such as potential temperature, salinity, density, and oxygen content no variation within the bottom waters surrounding the few living corals has been observed. Bottom waters show only minimal variation of the physical parameters across tidal cycles in the vicinity of the CAMV.

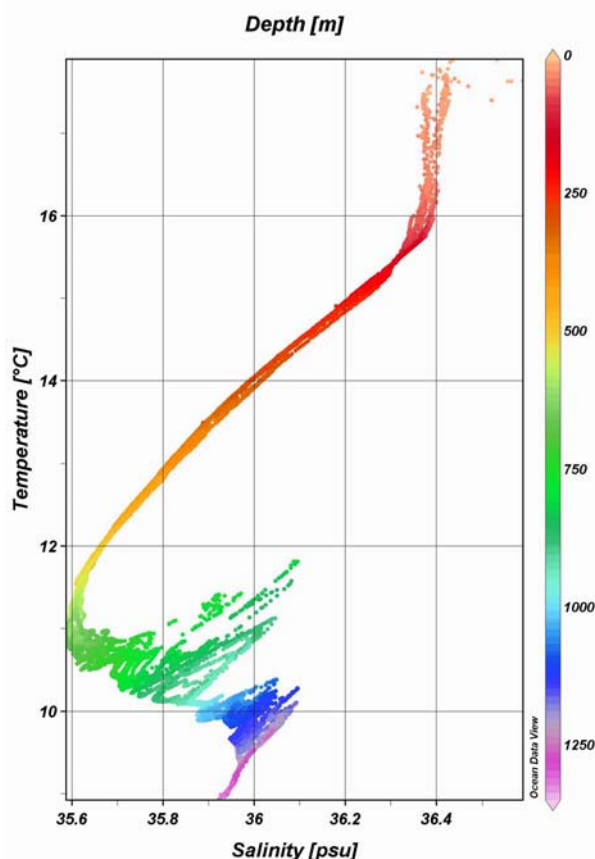


Fig. 2: T/S plot from Captain Arutyunov MV.

At the Mercator MV, sediment was sampled at the only gas bubble site reported so far in the area of the Gulf of Cadiz. The occurrence of gas bubbles could be confirmed by our OFOS observations. The pore water showed an extreme enrichment of Cl^- and SO_4^{2-} (Fig. 3) which are amongst the highest reported for mud volcanoes. Bottom water concentrations start at values only slightly higher than normal seawater, but rapidly increase below the surface to more than 8000 mM of chloride at a sediment depth of 200 cmbsf. Sulphate concentrations at the Mercator MV show a sulphate maximum at about 100 cmbsf and are about 2-3 times higher than sea water concentrations throughout the gravity core. These elevated SO_4^{2-} levels coincide with findings of gypsum in the core. The distinctive curvature in the Cl^- profile is indicative for quite rapid fluid ascent compared to the other mud volcanoes investigated in the previous weeks. The advection rate was preliminarily estimated to be in the order of 2 cm/a using simple transport-reaction modelling (see solid line in the Cl^- plot in Fig. 3). Potential sources for the chloride and sulphate are halite and gypsum dissolution, respectively.

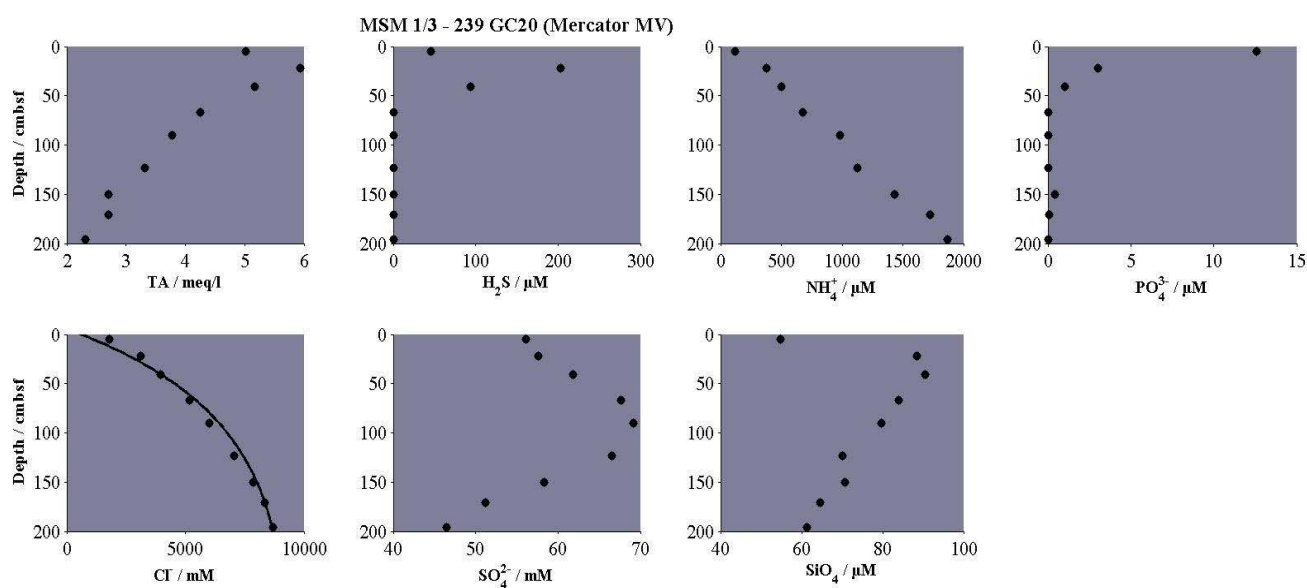


Fig. 3: Porewater profiles of a gravity core at a gas bubble site of the Mercator MV.

Mud volcanism represents an important pathway for fluids and gases from deeper reservoirs. Although several studies about the geochemistry and biology of mud volcanoes in the Gulf of Cadiz have been conducted, their activity in terms of methane emission into the water column and associated biogeochemistry has been only very poorly constrained.

Seabed methane emission, turnover and flux rates of oxygen, sulfate, sulfide, nitrate and ammonium are measured in situ using the Biogeochemical Observatory, BIGO, and the Fluid Flux Observatory, FLUFO. Parallel investigations are conducted using the TV-Multicorer, DOS (Deep Sea Observation Lander) BWS (Bottom Water Sampler Lander) and OFOS. BIGO and FLUFO are equipped with two benthic chambers each, which are driven into the sediment also enclosing a certain volume of overlying water from which at defined time intervals water samples are taken during the measurements. At the end of the measurements the sediment is retrieved by the observatories for later pore water analyses (Fig. 4).

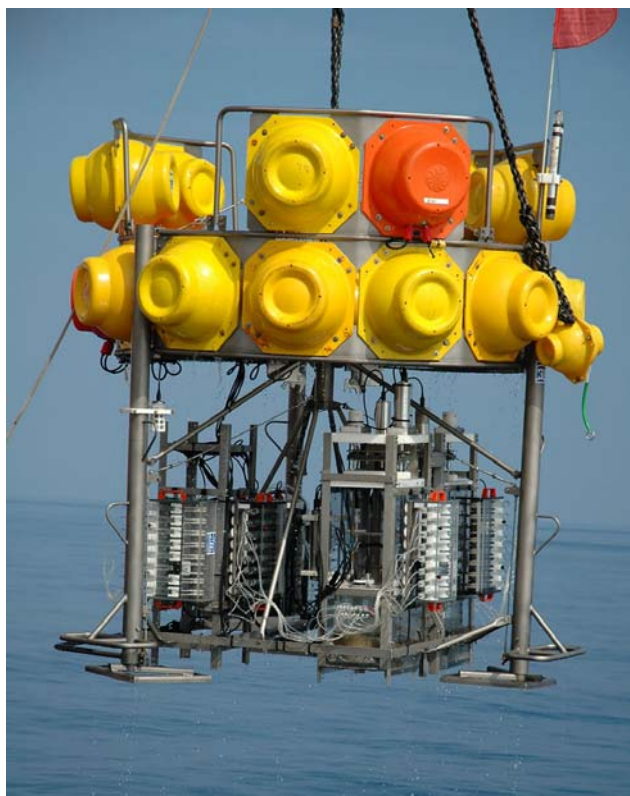


Fig: 4: Retrieval of the BIGO Lander with two mesocosms containing sediments.

From the water samples the time course of the concentration of methane, oxygen, sulfate, sulfide, nitrate, ammonia, pH and total alkalinity is deduced allowing the calculation of interfacial fluxes. Although the chambers are driven very slowly into the sediment instantaneous release of methane and other solutes into the overlying water column can occur. Thus, briefly after the chambers of BIGO have been driven into the sediment the chamber water is exchanged with ambient sea water to establish natural conditions for the start of the measurement. During the deployment the so called “Control” (CO) chamber of BIGO is flushed with ambient seawater at several time periods. By this means it is possible to measure seabed methane emission and other fluxes with a defined temporal resolution inside the same chamber. The second chamber of BIGO, further referred to as “Exchange” (EX) chamber is equipped with a gas exchange system (“Kieme”). This system maintains the oxygen level inside the Exchange chamber at the out-side level or it can be set to a defined oxygen concentration. Since the release of many solutes from the sediment is redox-sensitive, this system allows to measure fluxes at stable natural conditions or to conduct experiments under different oxygen tensions.

During the past weeks the mud volcanoes Bonjardim, Porto, Carlos Ribeiro, Captain Arutyunov and Mercator have been investigated. The biogeochemistry group focused their activity on CAMV where we found gas hydrates near the sediment surface. At all mud volcanoes distinct biological chemotrophic communities of bivalve molluscs and different species of tube worms are present. With respect to the occurrence of methane in the upper 30 cm layer of the sediment a wide range of methane concentrations were found (Fig. 5). Lowest concentrations were measured at Bonjardim MV and Porto MV, whereas highest concentrations were found at Carlos Ribeiro MV and CAMV. Within site variability is very high thus methane concentrations vary considerably. At almost all studied mud volcanoes elevated methane concentrations were not found at the surface of the sediment, except at CAMV in BIGO 2 CO_PL_1 (Fig. 5), where methane concentrations of up to $40 \mu\text{mol.l}^{-1}$ sed. were detected in the uppermost sediment layer. At this site we also detected high methane concentrations in the benthic boundary layer with a maximum of 687 nmol.l^{-1} at about 7cm above the sea floor (BWS #4, Fig. 6, indicating seabed methane emission. CTD casts at this site revealed maximum methane concentrations of 16 nmol.l^{-1} about 4 m above the sediment surface (Fig. 7). The background methane concentration in this area is 2.5 nmol.l^{-1} .

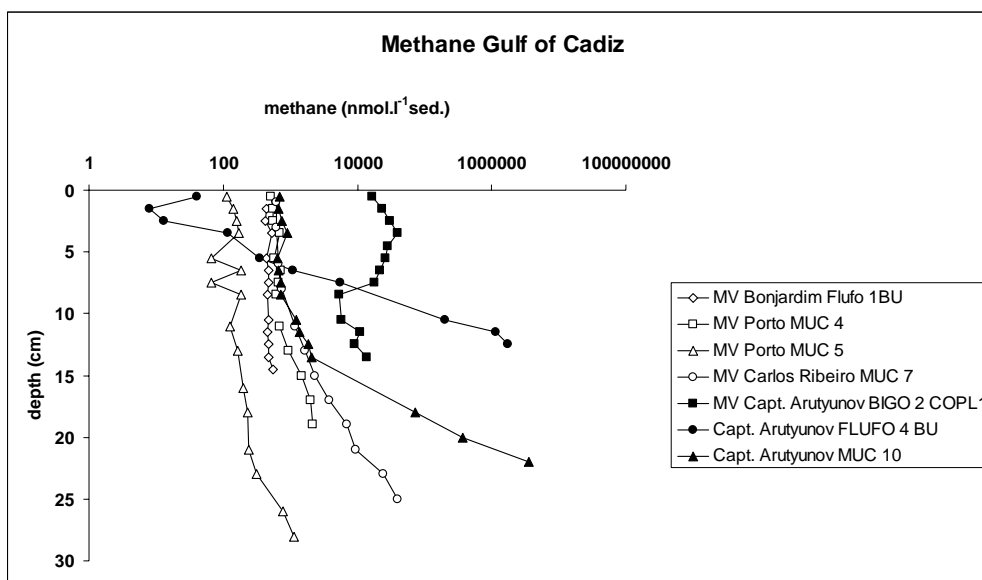


Fig: 5: Methane concentrations (log scale) in the uppermost 30 cm of the sediment at different mud volcanos in the Gulf of Cadiz.

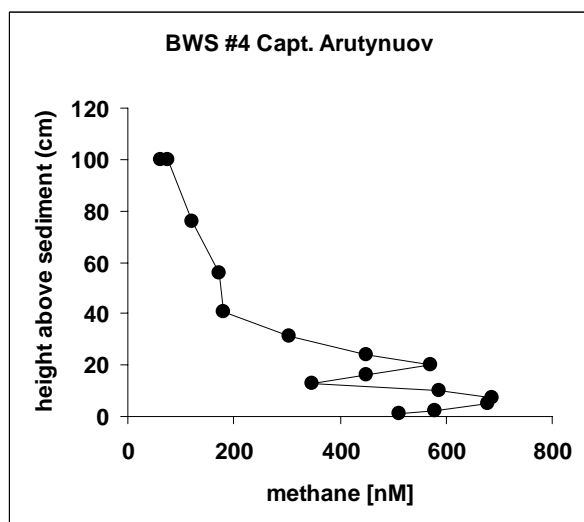


Fig: 6: Vertical methane concentration profile in the benthic boundary layer at the mud volcano Captain Arutyunov.

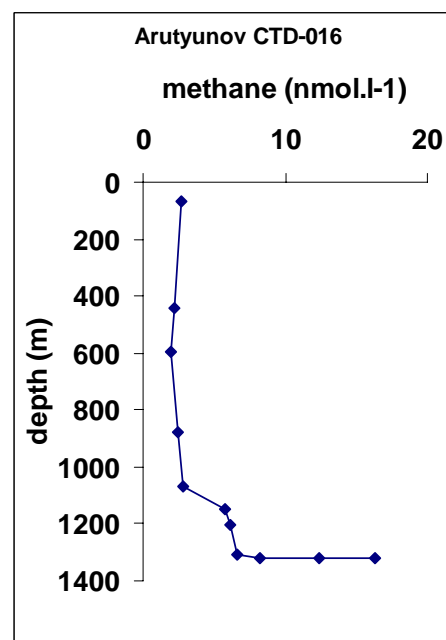


Fig. 7: Methane concentration in the water column above Arutyunov mud volcano.

At CAMV two BIGO (BIGO #1/#2) and one FLUFO (FLUFO #4) deployments were conducted for about 50 – 69 hours. Operation of the observatories was perfect. The gas exchange system deployed in BIGO to compensate oxygen consumption inside the benthic chamber (EX chamber) worked perfect and maintained the oxygen level inside the chamber at the defined level of 160 $\mu\text{mol.l}^{-1}$ over the entire time period of the measurement (Fig 8). At defined time intervals the water enclosed by Control chamber was exchanged with the ambient sea water to re-establish ambient natural conditions. By these means interfacial fluxes at different time intervals can be measured inside the same chamber. Oxygen consumption inside the control chamber is similar during the different time intervals. The noisy oxygen signal during the 3rd and fourth time interval is due to a failure of the stirring mechanism. During these measurements water samples for the later determination of methane, oxygen and other solutes

were taken at defined time intervals from inside the chambers (Fig 9). Additional samples were taken from the bottom water to monitor ambient conditions. From these water samples and the sediments retrieved by the benthic chambers Radon measurements were conducted, which will allow to reconstruct fluid flow rates.

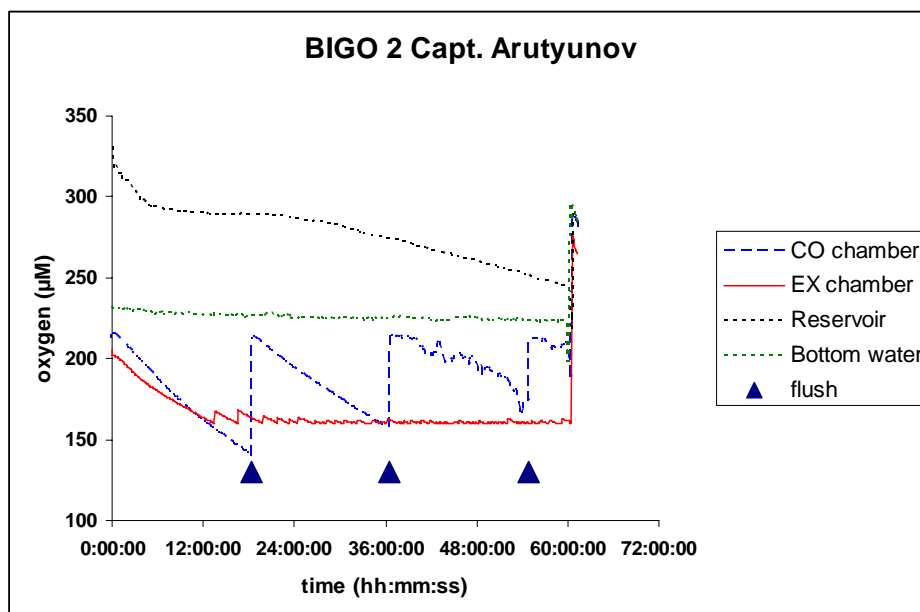


Fig. 8: Time course of the oxygen concentration inside the benthic chambers (EX and CO), the reservoir and the bottom water during deployment BIGO #2. The EX chamber is equipped with a gas exchange system. Oxygen is provided to this chamber from a reservoir containing filtered oxygen saturated sea water. At several time intervals (see triangles) the water inside the CO chamber was exchanged with the ambient bottom water.

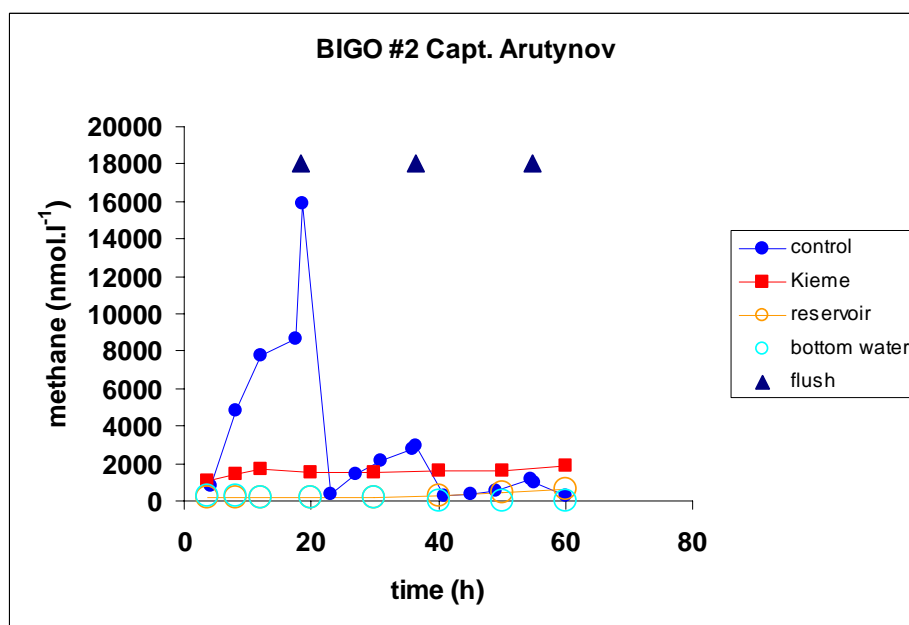


Fig. 9: Time course of the methane concentration inside the benthic chambers, the reservoir and the ambient bottom water during deployment of BIGO #2. Time periods, where the water inside the CO chamber was exchanged with ambient bottom water are indicated by triangles.

The diverse, presence of subsurface methane at CAMV appears to be correlated with the occurrence of extremely high abundances of pogonophores, probably of the genus *Siboglinum*, (Fig. 10), bivalve mollusks of the genus *Thyasira* and clasts (Fig. 11a-d).



Fig. 10: Bundles of pogonophorans (red bundles) sticking out at the base of the benthic chamber of FLUFO #4. They form dense forests on the surface of the sediments (see also Fig. 11)



Fig. 11: a. Bundles of tubes of *Siboglinum* sp.; b. living bivalve mollusk of the genus *Thyasira*; c. sparite (Kalkspat); d. clast, the stripes on clast shown in plate d might be caused from pogonophoran tubes. Samples are taken from different gears at MV Capt. Arutyunov.

Pogonophorans of the genus *Siboglinum* have been also described from methane seepage sites in the central Skagerrak (*S. poseidonii*) or from organically highly enriched sediments in fjords of Norway and Sweden (*S. ekmani*, *S. fjordicum*). They live in long tubes. They do not possess a mouth and gut openings. Instead of the presence of the digestive tract, the interior of *Siboglinum* carries a long sac like trophosome filled with chemosynthetic endosymbiotic sulfide- (*S. ekmani*, *S. fjordicum*) or methane- oxidizing bacteria (*S. poseidonii*). The posterior ends of the pogonophores extend out from the sediment into the oxygenated bottom water (Fig.12).

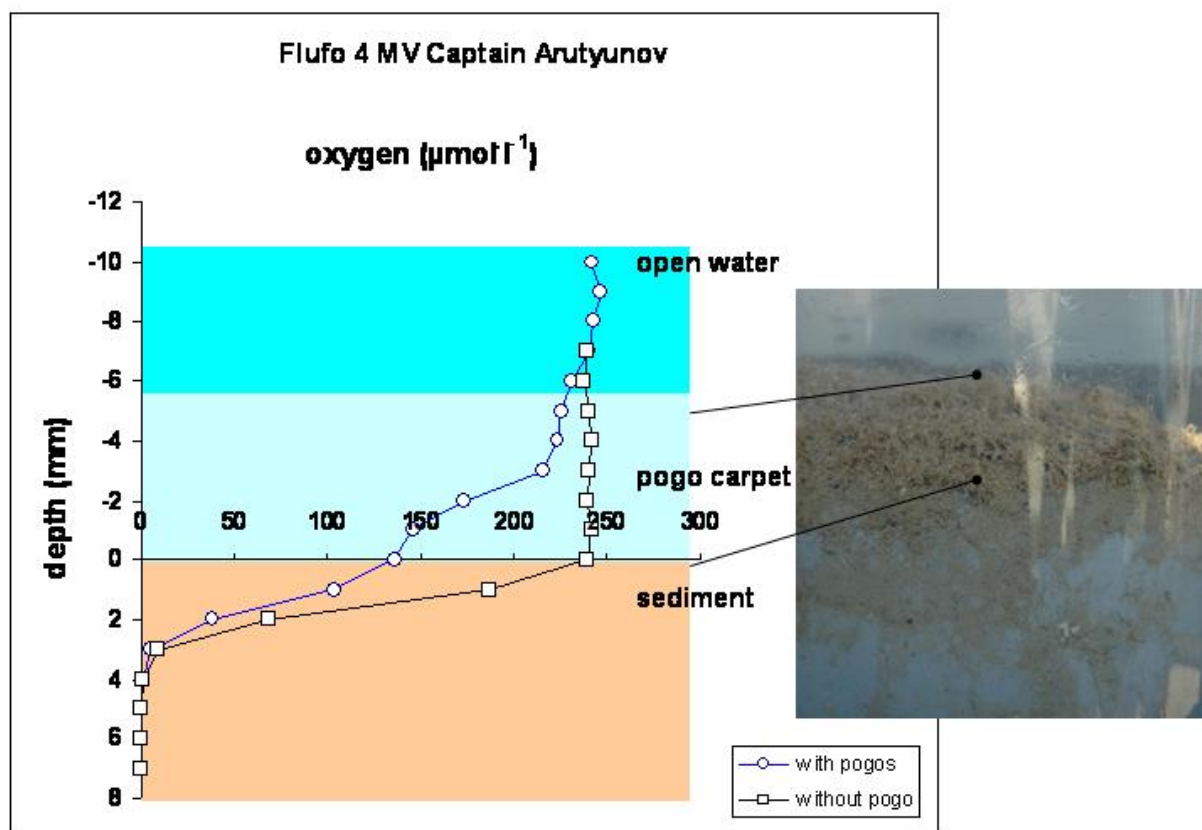


Fig. 12: Oxygen micro-profiles in sediments densely covered with pogonophorans (circles) in comparison to a location a few centimeters away with bare sediment (quadrats) (FLUFO #4). Photo insert shows vertical view of the benthic chamber of FLUFO #4.

The anterior end of the pogonophoran tubes penetrates deep down into the sediment. There the tube might be connected to sediment horizons with increased methane and sulfide concentrations, which are needed by the pogonophorans for their chemotrophic endosymbionts. During slicing the sediment cores from CAMV (FLUFO 3 Flux, MUC #9, MUC #10, BIGO 2 EX/CO) a smell of sulfide was detected in deeper sediment layers. Although dissolved sulfide was not detected in the upper 13 cm of the sediment core in FLUFO #4, elevated methane concentrations of $>200 \mu\text{mol.l}^{-1}$ sed. were measured at a depth of 10 cm. We can only speculate whether the chemotrophic endosymbionts of these pogonophorans depend on the supply of methane or sulfide. Anaerobic oxidation of methane which represents a major process in the methane turnover in seep sediments of the Gulf of Mexico and Hydrate Ridge releasing high levels of sulfide into the pore water apparently is not active at the seep sediments of CAMV, but there is a strong need for further microbiological investigations.

The tubes of the pogonophorans might represent ideal escape pathways for methane from deeper sediment layers into the water column. However, only very little methane has been released from this sediment into the overlying water column during FLUFO #4 deployment. In contrast to the methane measurements Radon show the highest concentrations ever measured

in this sea area. This points to the likelihood that Uranium is enriched in the anoxic sediment associated with the pogonophores. It is likely that the pogonophorans, their endosymbionts but also microbes attached to their integument control methane flux through these tubes. The high abundances of pogonophorans create a dense “forest” extending about 5 to 7mm into the water column. In this zone we measured lower oxygen concentrations than in the upper water column (Fig. 12). Probably this forest creates its own micro-climate which might further affect flux of methane and other solutes.

Our findings demonstrated that the Gulf of Cadiz mud volcanoes are highly different in comparison to the seep environments of the Hydrate Ridge or the Gulf of Mexico. We had to learn to think on different scales and concentration ranges, but we observe fascinating methane driven environments with distinct biological communities.

An Bord sind alle wohlauf.

Es grüssen.

O. Pfannkuche und alle Fahrtteilnehmer